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Performance characteristics of concrete based on a ternary calcium sulfoaluminate–anhydrite–fly ash cement



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ABSTRACT

This paper reports an assessment of the performance of concrete based on a calcium sulfoaluminate–anhydrite–fly ash cement combination. Concretes were prepared at three different w/c ratios and the properties were compared to those of Portland cement and blast-furnace cement concretes. The assessment involved determination of mechanical and durability properties. The results suggest that an advantageous synergistic effect between ettringite and fly ash (Ioannou et al., 2014) was reflected in the concrete's low water absorption rates, high sulfate resistance, and low chloride diffusion coefficients. However, carbonation depths, considering the dense ettringite-rich microstructure developed, were higher than those observed in Portland cement concretes at a given w/c ratio. It was concluded that the amount of alkali hydroxides present in the pore solution is as important factor as the w/c ratio when performance of this type of concrete is addressed.

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1. Introduction

Due to a combination of an energy-intensive process and calcination of raw materials during manufacture of Portland cement (PC), the embodied CO₂ emissions (eCO₂) of concrete are mainly affected by the cement content rather than any of the other constituents. Due to increasing pressure to reduce the eCO₂ of concrete [2,3], industries across the globe are focusing on alternative approaches for the production of more sustainable cement combinations. Among these approaches, replacement of PC with non-Portland cement based materials is a feasible scenario. Among the most promising non-Portland cements, possessing potentiality for commercial-scale production, are the calcium sulfoaluminate cements. Calcium sulfoaluminate cement (CSAC) is obtained by burning a mixture of limestone, bauxite (or an aluminous clay) and gypsum at 1300–1350 °C in rotary kilns [4]. As this is 100–150 °C lower than that involved in PC production, the energy input requirement is therefore lower. Since the manufacturing process is similar to that of PC, energy consumption savings reach approximately 15–30 kW h [5]. Based on the eCO₂ emissions associated with the individual mineralogical cement compounds [6],

and given that a typical CSAC consists of predominantly ye'elimite, belite and smaller amounts of aluminoferrite, then the eCO₂ of CSAC can be estimated at approximately 600 kg/t, which is up to 35% lower than that associated with PC.

There is a considerable body of research available on the hydration and microstructural aspects of CSAC-based cements [1,4,5,7]. The main hydration product is ettringite, which is formed at early stages upon reaction between ye'elimite and calcium sulfate (added externally if not interground during manufacturing) in the presence of water. The phase is fundamental for the properties of the concrete, such as high early strengths, dense matrix and durability. When ye'elimite reacts with an insufficient amounts of calcium sulfate, then monosulfoaluminate is formed, whereas in the case of reaction with excess calcium sulfate, then the system is likely to be dimensionally unstable. Therefore one of the important factors underpinning performance and durability of CSAC/anhydrite combinations is the relationship between ye'elimite content and calcium sulfate content.

Although the hydration mechanisms of CSAC/anhydrite cements have been extensively studied over the past decades [7], there has been, however, little consideration of the long term durability of CSAC/anhydrite-based concretes, at least towards assessing their applicability for commercial scale use under standardized procedures. In this regard, there is a need to evaluate

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the true potentiality of the combination prior to introducing them to current design frameworks.

Concretes based on a CSAC/anhydrite cement have been determined to have relatively high early strengths, in the range of 40–50 N/mm² at 7 days at typical w/c ratios. The high early strength is primarily due to the formation of ettringite during hydration [8–10] and thereafter strength gain is slower than in Portland cement concretes to equivalent 28-day strengths.

Quillin [9] found that CSAC/anhydrite concrete exhibited excellent sulfate resistance although carbonation depths were higher than those of Portland cements and chloride diffusion coefficients were relatively high. Kalogris et al. [10] studied the influence of synthesized non-expansive CSAC/anhydrite cement on the steel reinforcement corrosion. They found reducing pH values in the pore solution, falling from 8.5 to 6 within 2 to 3 weeks of exposure to NaCl solution or tap water. When CSAC/anhydrite concrete was exposed to intermittent exposure to 3.5% NaCl solution they observed a high averaged corrosion rate of reinforcement and increasing Cl⁻ ion concentrations. Carbonation depths of CSAC/anhydrite concretes removed from service were determined using infrared spectroscopy [11]. It was found that the carbonation of normal CSAC/anhydrite concrete averaged at about 0.5 mm/year and that the concrete sample removed from the high strength pile carbonated at a rate of 60 µm/year. The high resistance was attributed to self-desiccation of the matrix. Zhang [12] investigated the chloride resistance of a 16-year in-service concrete pipe using Electron probe Micro analysis and Quantab chloride titrator strips. He concluded that the chloride resistance of the concrete was very high and observed that the embedded steel reinforcement in the pipe was smooth and intact. Dachtar [13] studied the chloride permeability through electrical conductivity of CSAC/anhydrite concretes. Compared to PC concretes they exhibited less electrical resistivity due to their low alkali content and lower pH values.

An aspect to be addressed is that of the availability of the raw materials in a CSAC/anhydrite cement for potential commercial-scale production. Bauxite deposits are unevenly distributed and, compared to limestone, the resources are not as abundant [14]. Impure alumina and anhydrite resources are nonetheless fairly widespread. This might increase the potential for large-scale production of CSAC should the manufacture be based on impure alumina resources, as is the case in China [14].

A further aspect to be considered is the eCO₂ emissions of the cement. A CSAC with no additional gypsum appears to be associated with eCO₂ values that may not seem low enough to make substantial reductions when considering such a cement combination for commercialization. In fact, the approximate value of 600 kg/t as determined for CSAC is even higher than the average values of conventional blastfurnace cements. Therefore, to strengthen the potential to offer substantial eCO₂ reductions for achieving equivalent concrete performance there is a definite need to develop a

chemically stable and dense CSAC/anhydrite combination that makes maximal use of additions.

In this paper, an experimental study was carried out to assess the long term performance of concrete using a novel calcium sulfoaluminate/anhydrite/fly ash combination that has been proven in earlier work to have suitable cementitious characteristics [1]. The concrete is compared with reference Portland cement-based concretes. The assessment involved determination of fresh, mechanical, permeation and durability properties and a discussion on the applicability of the concretes to current design codes is provided.

2. Materials and methods

The experimental programme included a comparison of concretes based on three cement types: (i) a Portland cement (CEM I), (ii) a blastfurnace cement combination (III/A) and (iii) a calcium sulfoaluminate–anhydrite–fly ash cement combination that was developed in previous work [1]. Characterization and mix proportioning of the combinations are shown in Table 1. For the preparation of concrete mixes, crushed limestone aggregates were used as the coarse aggregate of sizes 4/10 mm and 10/20 mm. A combination of Marlborough grit and fine alluvial sand at a 1:1 ratio to achieve a medium grading requirement (MP), as in BS EN 206:2013 [15] was used as the fine aggregate in the concrete mixes. PSD of all aggregates are given in Fig. 1 and description is given in Table 2.

All concretes were prepared at w/c ratios of 0.35, 0.50 and 0.65. CEM I concretes were proportioned according to the BRE method for designing normal concrete mixes [16] for achieving a consistency conforming to the S2 slump as in BS EN 206:2013. In all mixes, a polycarboxylate based superplasticizer was added in the mix at 2% by mass. To maintain validity in comparison, the remaining concrete mix proportions were obtained by: (i) maintaining the same water, cement/combination and coarse aggregate content (kg/m³) for all concretes and (ii) adjusting the fine aggregate content (kg/m³) to maintain the volumetric yield based on the known densities of the constituents used [1].

Concrete mix proportions are shown in Table 3.

Mixing of concrete was carried out in accordance with BS 1881-125:2013 [17]. Samples were demoulded after 24 h and water-cured at 20 °C until specified ages of testing.

Consistence of fresh concrete was determined as a slump according to BS EN 12350-2:2009 [18], and the compressive strength development of 100 mm cubes was measured in accordance with BS EN 12390-3 [19].

The static elastic modulus of concrete was determined in accordance to BS 1881-121:2013 [20] using 300 mm long by 150 mm diameter cylinders. The test was performed on a load-control basis

Table 1
Constituent properties and combination proportioning.

Constituent description	CEM I conforming to BS EN 197-1:2000	Ground granulated Blast furnace slag to BS EN 6699:1992	Calcium sulfoaluminate cement	Commercially available anhydrite	Fly ash category N conforming to BS EN 450-1:2012
Constituent notation	CEM I	Ggbs	CSAC	ANH	FA
Particle density	3140	2900	2790	2950	2290
Mean diameter size	19.6	18.6	25.3	24.5	34.5
Particle size distribution					
d ₁₀	1.7	1.6	2.2	2.3	2.4
d ₉₀	38.3	40.2	64.8	42.1	81.6
Cement notation	Mix proportions (% by mass)				
CEM I	100	0	0	0	0
III/A	50	50	0	0	0
GAF15	0	0	55	30	15

with a stress rate of 0.5 N/mm^2 for all cycles including the final linear ramp to failure.

Carbonation resistance of hardened concrete was measured in accordance to the European Standard CEN/TS 12390-12:2010 [21]. The $300 \times 75 \times 75 \text{ mm}$ samples were initially conditioned for a period of 14 days and then water cured at 20°C for 28 days. The carbonation chamber was set to 4% CO_2 atmosphere, temperature of 20°C and 65% RH. Longitudinal slices of 50 mm were cut from the sample at weekly intervals for the determination of carbonation depths, which involved the use of phenolphthalein solution in the internal surface of the slices.

Water absorption of concretes was determined using a method based on that described in ASTM C 1585-04 [22] with the exception of using rectangular cross section samples of $150 \times 150 \times 50 \text{ mm}$. The surface tested was immersed in water depth of 3 mm. Measurements of mass were at intervals specified for up to 3 days. The water sorptivity was then determined ($\text{mm/s}^{0.5}$) by linear regression using the equation:

$$I = S_i \sqrt{t} + b \quad (1)$$

where I is the cumulative absorbed volume after time t per unit area of inflow surface, S_i is Water absorption rate (sorptivity) and t is time pass since commence of the experiment (seconds).

The chloride resistance of 100 mm concrete cubes was determined in accordance with the methods described in DD CEN/TS 12390-11:2010 [23] and in BRE Information Paper IP 21/86 [24]. Non-steady diffusion coefficients and surface chloride contents were obtained by linear regression.

The sulfate resistance of concretes was determined using the method proposed by Dhir et al. [25] which involves monitoring at two week intervals the change in length of 28-day water cured $300 \times 75 \times 75 \text{ mm}$ prisms, immersed in a 5% Na_2SO_4 solution at 20°C . This exposure is approximately 5.6 times stronger than the most severe environment in EN 206:2013. The solution was changed periodically, to maintain the concentrations through the immersion period. Sulfate expansions were monitored for a period of 40 weeks.

3. Results and discussion

3.1. Consistence

Slump values of concrete mixes at w/c ratio 0.35, 0.50 and 0.65 are shown in Fig. 2a–c. Values were obtained at 0, 5, 10, 15 and 20 min after the mixing process.

The addition of superplasticizer contributed to very good finishability characteristics of all concretes. Slump values of GAF15 concrete met the target S3 class and little effort was required for finishing. At lower w/c ratios the loss of slump for GAF15 concrete was greater than the reference mixes. A possible cause for this behaviour would be the formation of rich amounts of ettringite in the cement matrix. This sulfoaluminate phase is characterized by a high water demand [26] as 32 H_2O molecules are bound according to the chemical formula. Upon immediate formation of the needle-like crystals, higher amounts of mixing water were absorbed in GAF15 and therefore the fluidity was reduced when compared to that of reference mixes.

3.2. Cube strength

The cube strength development of concretes at w/c ratio of 0.35, 0.50 and 0.65 is shown in Fig. 3a–c respectively. Strength development of concretes as a percentage of the 28-day strengths is shown in Table 4.

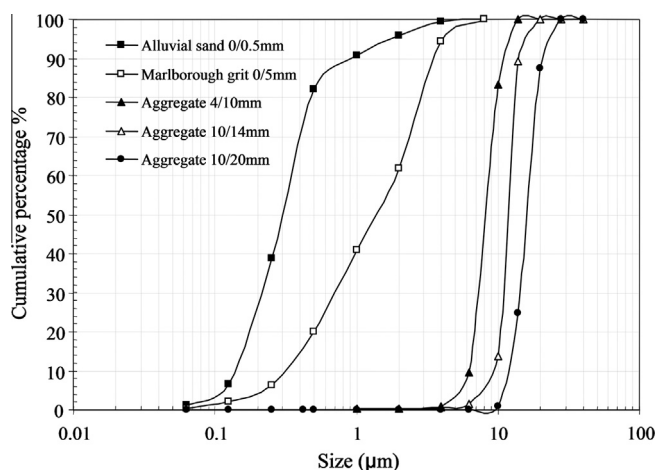


Fig. 1. PSD of aggregates used in concrete mixes.

The 28-day cube strength of GAF15 was similar to that of both CEM I and III/A concretes for a given w/c ratio. At lower w/c ratios, GAF15 concrete exhibited the lowest cube strength, approximately 2 N/mm^2 and 4 N/mm^2 lower than CEM I and III/A concretes respectively. However, at a w/c ratio of 0.65 GAF15 concrete showed the highest strength values as a result of the less steep trend. There are several explanations for this behaviour and the hydration mechanisms of each system need to be considered. In CEM I, C–S–H is the main binding phase responsible for the strength development. It is known to possess a high surface area and adhesive capability. Because of the van der Waals forces of attraction existing in the hydrated cement, C–S–H phases and other hydration products tend to adhere not only to each other, but also to solids that have low surface area, such as anhydrous clinker and the aggregate. During setting, the paste maintains a stable volume which is approximately equal to the sum of volume of cement and of water [27]. In a hydrated CSAC/anhydrite cement, the ettringite crystals similarly tend to adhere to each other and to the anhydrous particles (aggregates), however, because, of their large size and morphology [1], the interlocking effect is an additional factor that plays an equally important role. Moreover the presence of high amounts of ettringite needles with unreacted FA particles firmly wedged within the formed sulfoaluminate phases [1] ensured a dense microstructure in each case.

The GAF15 concrete continued to gain strength beyond 28 days, with the strength at 180 days approximately 6–8% higher than the 28-day strength (Fig. 3a–c). This behaviour is associated with the perseverance of ettringite within the fly-ash void filling mechanisms. The particular increase however, was lower than those observed in the reference concretes, probably due to the ongoing formation of C–S–H in the PC concretes whereas in GAF15 the anhydrite had already been fully consumed at early hydration stages and no more ettringite might have been formed thereon. At 7 days, GAF15 cube strengths reached approximately 86–95% of their 28-day (Table 3) indicating that early strengths are a characteristic of CSAC/calcium sulfate-based combinations.

3.3. Elastic modulus and cylinder strength

Static modulus of elasticity in compression E_{cm} and cylinder strengths f_{ck} obtained from the experimental analysis, are shown in Fig. 4.

The relationship between w/c ratio and elastic modulus for all concretes tested was inversely proportional, although a steep increase in GAF15 at w/c ratio of 0.35 was observed. GAF15

Table 2
Properties of aggregates used in concrete mixes.

Aggregate	Type	Size	Specific gravity	Water absorption, % by mass
Crushed limestone	Carboniferous	10/20 mm 10/14 mm 4/10 mm	2.7	0.6
Marlborough Grit	Alluvial	0/4 mm	2.65	0.6
Fine Sand		0/0.5 mm		

concretes exhibited the highest modulus of elasticity with a difference of approximately 2–5 kN/mm² from the III/A concretes. The reasons for this are partly based on the explanations described in the previous section. Fundamentally, the reference concrete may be regarded as a three-phase composite material consisting of the cement paste, the aggregate and the interfacial transition zone between the two. Consequently, the main factors determining the elastic modulus would be the aggregate properties (porosity, size, content, shape, and surface texture), the cement paste properties (mainly porosity) and the composition of the interfacial transition zone [27]. Since in this study the aggregate maximum size was kept constant and the aggregate content was only slightly varying with w/c ratio, it may be assumed that the behaviour of stress strain curves of concretes at a given w/c ratio could be explained to a major extent by the binding mechanisms within the cement paste.

The formation of ettringite and its co-existence with tightly accommodated FA particles in GAF15 [1] clearly contributed to higher values of elastic modulus compared to III/A and CEM I. In CEM I the tendency of C–S–H to adhere to aggregates (and to other low surface-area solids) is the main factor that defines the curvature in stress–strain relationship. In GAF15, however, ettringite has an additional interlocking characteristic in addition to this tendency, due to their crystalline size, structure and morphology and therefore load dependent deformations occurred to a lesser extent.

3.4. Sulfate resistance

Sulfate expansion strains of concretes at w/c ratios of 0.35, 0.50 and 0.65 are shown in Fig. 5a–c. The relationship between 40-week expansion strains and w/c ratio are shown in Fig. 6.

For all w/c ratios, GAF15 concretes exhibited the lowest expansions throughout the 40-week test period. Strains at 40 weeks for GAF15 were approximately $20\text{--}40 \times 10^{-6}$ lower than those of

III/A concrete. This is as a result of aluminate-bearing phases being bound in the ettringite phase (formed when concrete was still in the semi-plastic state) and unavailable for reacting with external sulfates to form expansive sulfoaluminates in the hardened paste [11]; secondly, from observation of the microstructure of this particular cement combination in our previous work [1] the addition of FA to a CSAC/anhydrite combination further reinforces the resistance to ingress of sulfates, as a dense matrix is promoted.

Expansions of concretes were generally less than 200×10^{-6} at all w/c ratios and initiation occurred at approximately the 4–6th week of immersion at higher w/c ratios. CEM I concrete showed the highest sulfate expansion values, and the cause of the high values would be the presence of available tricalcium aluminates that instigated formation of expansive ettringite [27]. A proportional yet not precise relationship was noted between w/c ratio and sulfate expansion for all concretes as shown in Fig. 6 and no cracking was observed in any concrete during 40 weeks of exposure. The results suggest that the introduction of CSAC/anhydrite/FA concrete within current standardized procedures in concreting practice may be applicable, given the sulfate concentration in which the samples were exposed.

3.5. Carbonation resistance

Carbonation depths of concretes measured throughout period of 7 weeks at w/c ratios of 0.35, 0.50 and 0.65 are shown in Fig. 7a–c. The relationship between the 7-week carbonation depths obtained and w/c ratio is given in Fig. 8 and the relationship between 7-week carbonation depths and 28-day cube strengths is shown in Fig. 9.

Resistance of all concretes to carbonation reduced with an increase in w/c ratio and for GAF15 concrete the depths at 7 weeks increased significantly with an increase in w/c ratio. The results show that depths for GAF15 concrete were higher than for both other concretes at all w/c ratios during the test period. For a given cube strength, carbonation resistance of GAF15 was poorer (Fig. 9), indicating that the dense microstructure developed by ettringite and firmly accommodated fly ash particles is not a parameter that significantly influences the resistance to carbonation. This behaviour reflected that the carbonation-impeding alkalis in the pore solution may underpin an equally significant role in carbonation resistance.

CEM I and III/A concretes exhibited the lowest depths throughout all weeks of examination. The slightly higher values in III/A concrete was probably due to partial consumption of the alkali hydroxides by the ggbs. The process of carbonation in Portland cement concrete has been extensively described, among numerous authors, in [28–30] and occurs because the amounts of formed $\text{Ca}(\text{OH})_2$ within the hydrated Portland cement are crucial for

Table 3
Mix proportions of concretes.

Cement	w/c	Water (l/m ³)	Cement (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate	
					4/10 mm kg/m ³	10/20 mm kg/m ³
CEM I	0.35	190	545	580	375	745
III/A	0.35	190	545	560	375	745
GAF15	0.35	190	545	490	375	745
CEM I	0.50	190	380	660	390	785
III/A	0.50	190	380	650	390	785
GAF15	0.50	190	380	600	390	785
CEM I	0.65	190	290	755	385	770
III/A	0.65	190	290	745	385	770
GAF15	0.65	190	290	705	385	770

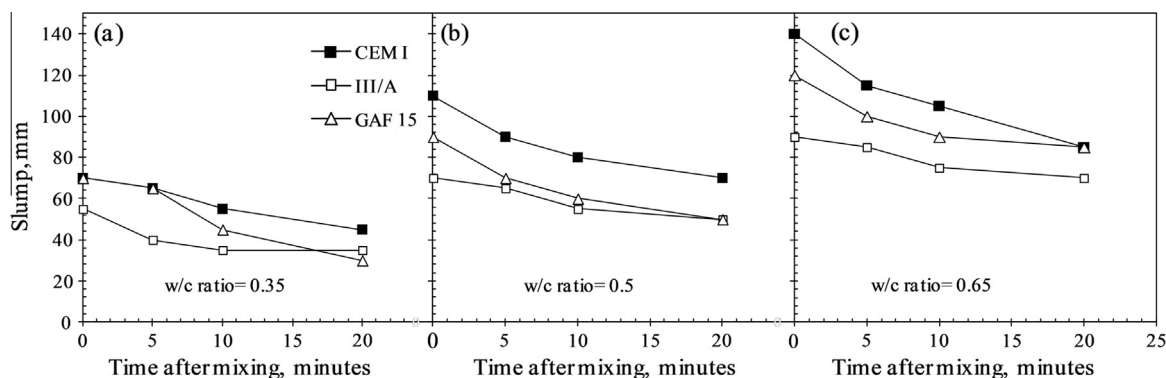


Fig. 2. (a–c) Slump of concretes at w/c ratio of (a) 0.35, (b) 0.5 and (c) 0.65.

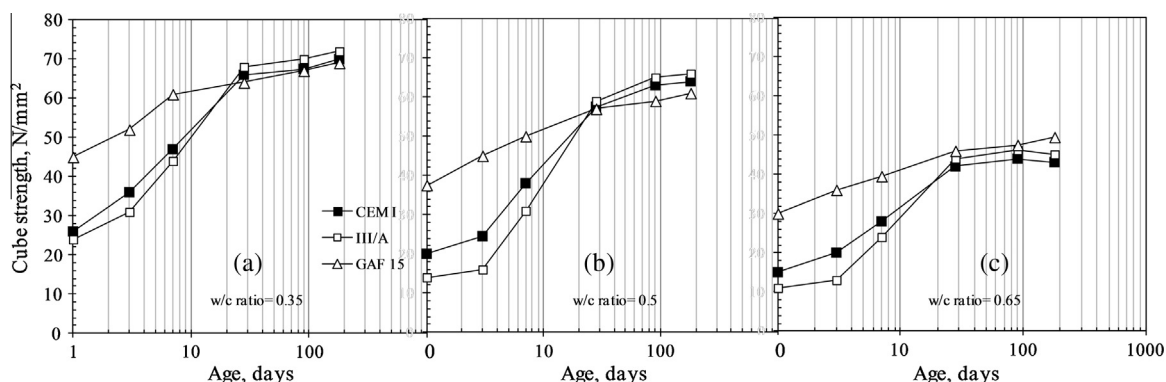


Fig. 3. (a–c) Cube strength development of concrete mixes at (a) w/c = 0.35; (b) w/c = 0.5 and (c) 0.65.

Table 4

Cube strength development of concretes as a percentage of 28-day strength.

Cement/ combination	w/c ratio	Days					
		1	3	7	28	90	180
CEM I	0.35	37.2	55.0	72.4	100	104.6	106.9
III/A	0.35	32.8	46.3	65.7	100	102.9	104.8
GAF15	0.35	70.0	82.3	95.6	100	103.6	108.6
CEM I	0.50	34.4	43.1	67.7	100	111.1	115.5
III/A	0.50	22.2	29.3	52.1	100	111.8	115.3
GAF15	0.50	66.3	79.9	88.9	100	102.8	106.3
CEM I	0.65	37.5	47.9	68.9	100	106.8	104.1
III/A	0.65	25.7	32.3	56.7	100	105.3	101.4
GAF15	0.65	65.4	78.6	86.8	100	104.3	108.4

maintaining high alkalinity in the system and impede carbonation. During diffusion of atmospheric CO_2 in concrete pores within the presence of moisture, carbonic acid is formed and, in reaction with the available $\text{Ca}(\text{OH})_2$, the resulting product is CaCO_3 . It is also suggested that C–S–H and unreacted C_2S and C_3S also participate in the reaction, similarly forming CaCO_3 [29,30]. With the reduction of available $\text{Ca}(\text{OH})_2$ amounts, the alkalinity in the system causes proneness to reinforcement corrosion and concrete exhibits reduced mechanical performance [31].

Hydration product studies on GAF15 suggest that no little or no $\text{Ca}(\text{OH})_2$ is available in the combination to impede carbonation and thus the predisposition of ettringite to carbonate is high [1]. Therefore, the carbonation resistance of the concretes would not only be strongly defined by the porosity and diffusivity aspects of concretes but also by the presence of alkali hydroxides. This characteristic is apparent at any w/c ratio as shown in Fig. 8. An important conclusion is that, the current hitherto practice of using the compressive strength in Portland cement concrete as an indirect

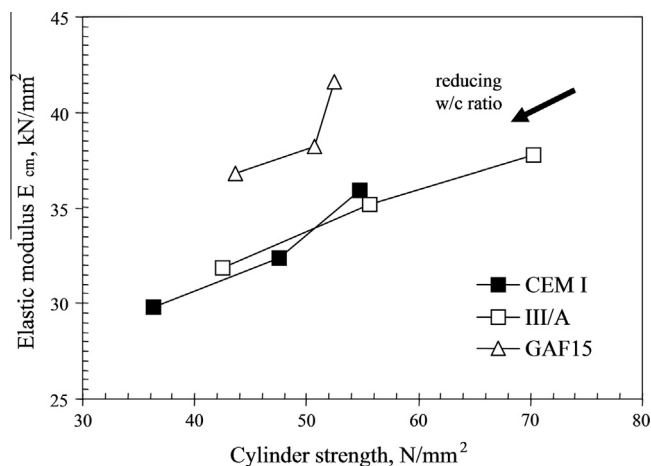


Fig. 4. Relationship between elastic modulus and cylinder strength of concretes.

indicator of its carbonation resistance would be misleading in the case of a CSAC/anhydrite/fly ash concrete because of such predisposition of the combination. Consequently, although a high-strength PC concrete may be associated with low carbonation depths, a high-strength CSAC/anhydrite/FA concrete may still exhibit relatively high depths.

3.6. Chloride resistance

Non-steady state diffusion coefficients, D_{NSS} , of concretes exposed to 3% NaCl solution for 90 days are given in Fig. 10.

The results showed a reduction in D_{ns} of GAF15 concretes for increasing cube strengths and decreasing w/c ratios. At a given w/c ratio, D_{ns} for the GAF15 concrete were approximately $1.7\text{--}6.8 \times 10^{-12} \text{ m}^2/\text{s}$ higher than those obtained from III/A concrete and approximately $6.8\text{--}10.3 \times 10^{-12} \text{ m}^2/\text{s}$ lower than those of CEM I.

The relative change in D_{ns} for GAF15 concrete was comparable to those of the reference mixes. There are probably two main reasons for GAF15 exhibiting a controllable behaviour. The first would be the beneficial effect from co-existence of ettringite with tightly accommodated unreacted FA particles. This effect is responsible for the dense microstructure of the matrix, thus the ingress of free Cl^- is reduced. The second cause would be the absence of calcium monosulfoaluminate. As reported in [1], sufficient amounts of anhydrite were introduced in the combination to prevent conversion of ettringite to monosulfoaluminate thus no additional chemical binding activities were developed to upset the coefficient values.

It is generally understood that the rate of ingress of external Cl^- ions into concrete depends on the interconnectivity of the pore network in concrete (i.e. permeability), the external chloride concentration, and environmental parameters such as temperature and relative humidity. Of additional importance is the chloride binding ability of the hydrated phases. This ability is typically expressed through chloride binding isotherms, i.e. the relationship between free Cl^- in the pore solution and bound chlorides in hydrated phases. In Portland cement, the C–S–H phase physically binds Cl^- ions due to its high specific surface. The process is based on a physical adsorption (exchange) mechanism. Chlorides tend to physically adsorb on the surface of the C–S–H phase through exchange between Cl^- ions existing in the pore solution and hydroxyl ions from the C–S–H layers [32], as the OH^- ion is loosely bound and therefore the external Cl^- ion is allowed to replace this.

It is unclear, however, whether the chloride binding mechanism associated with ettringite is based on physical adsorption or chemical substitution. There appear to be different findings in the literature that assign the phase either with a low or with a high binding ability [33,34]. It was also suggested [35] that the chloride binding capacity of ettringite is based on a mechanism which acts as a combination of chemical substitution and physical adsorption.

In this research, no studies on the microstructure and chemistry of GAF15 when immersed in NaCl solution have been conducted; therefore no conclusions can be drawn upon whether ettringite possesses the ability to bind chloride ions. However, an alternative approach to give an indirect indication of the mechanism is proposed. The method involved the determination of chloride diffusion coefficients yielded for concretes of equal absorption rate, as shown in Fig. 12. It was assumed that when all concretes are of equal water sorptivity, then the capillary pore interconnectivity

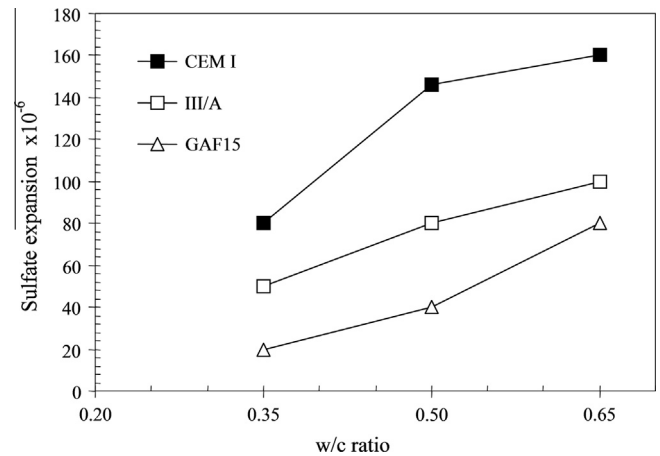


Fig. 6. Relationship between 40 week expansion strains and w/c ratio of concretes.

of concretes is similar – thus it was assumed that it was safe to eliminate this parameter. Therefore any significant differences in coefficients can then be indirectly explained solely by the chloride binding ability of the hydrated phases and not by porosity. This was followed on the grounds that the determined chloride diffusion coefficients, according to CEN/TS 12390-11:2010, were non-steady state coefficients, meaning that these values take into account the binding ability of the phases and that the flow of chloride ions was not constant during the time of the experiment. The observations are described under sorptivity in the next section.

The relationship between w/c ratio and D_{ns} for all concretes appeared to be proportional and values of coefficients did not exceed $45 \times 10^{-12} \text{ m}^2/\text{s}$. The results suggest that there is no additional risk of chloride-induced corrosion in a CSAC/anhydrite/FA concrete above that of using a PC-based concrete; given that a stable matrix is formed without incorporating any risks of phase conversions.

3.7. Sorptivity

Calculated rates of absorption S_i of concretes at w/c ratios of 0.35, 0.50 and 0.65 are shown in Fig. 11. Relationship between absorption rates and 28-day cube strengths/7-week carbonation depths –chloride diffusion coefficients are given in Fig. 12.

For all concretes, absorption rates were found to be proportional to the w/c ratios tested and GAF15 concretes exhibited controllable rates with comparable variations to those of III/A at increasing w/c ratios. At w/c ratios of 0.35 and 0.5, values were slightly higher than those of III/A. This characteristic may well reflect the synergistic void filling effect between rich amounts of

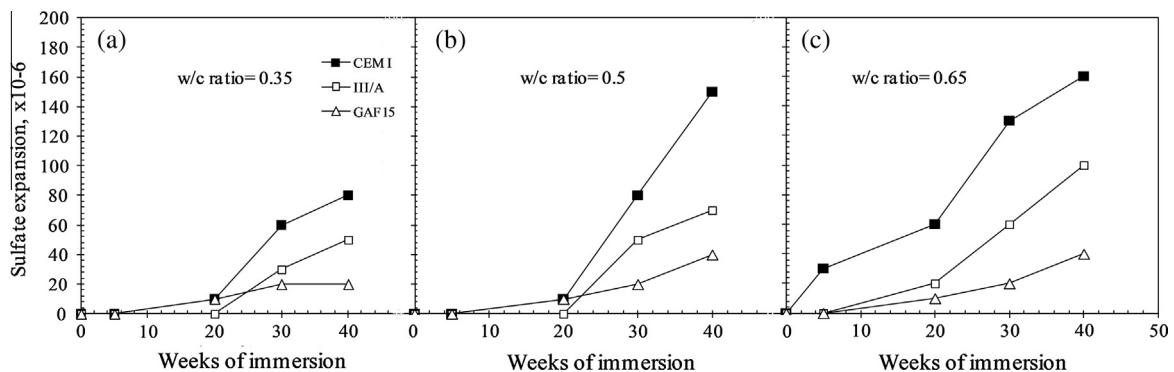


Fig. 5. (a–c) Sulfate expansion of concretes at w/c ratio of (a) 0.35; (b) 0.5 and (c) 0.65.

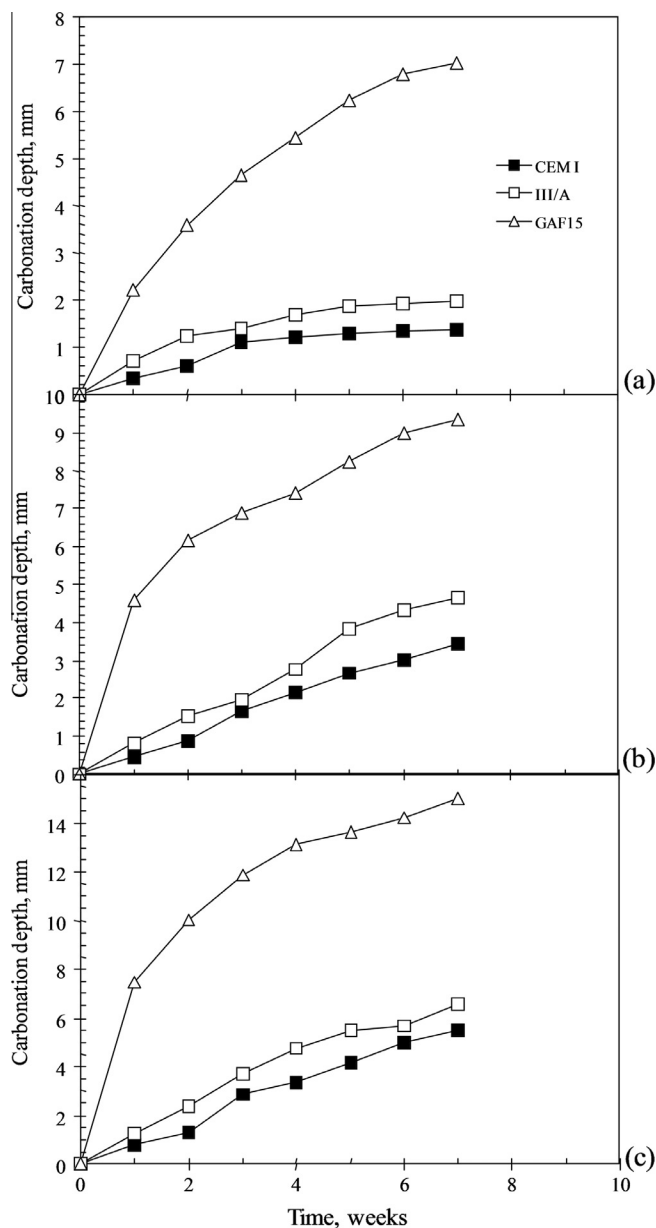


Fig. 7. (a–c) Average carbonation depths of concretes at w/c ratio of 0.35.

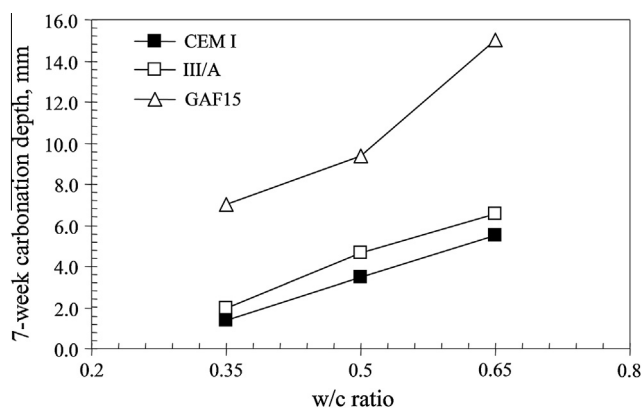


Fig. 8. Relationship between 7-week carbonation depths and w/c ratio of concretes.

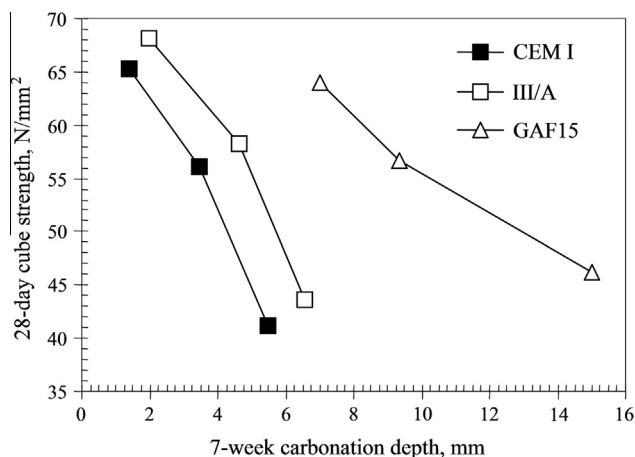


Fig. 9. Relationship between 28-day cube strengths and 7-week carbonation depths of concretes.

ettringite combined with firmly attached FA particles, all contributing to the discontinuity in the pore network.

Observation of the particular order of ascending chloride concentration in the pore solution gave an indirect indication of the binding abilities of the products. For concretes to achieve a similar capillary pore interconnectivity pattern, the sum both chemically bound and free chloride ion concentrations appears to be highest in GAF15 concrete, denoting that higher degree of chloride binding activities tend to occur at ettringite-rich environments than C–S–H based matrices, although conclusions cannot be made with certainty based on this method. When observing the relationship between carbonation depths and absorption rates (Fig. 12(b)), it can be seen that for all concretes to achieve equal water absorption the yielded carbonation depths were still higher than those of reference concretes.

3.8. Potential use of a CSAC/anhydrite/fly ash cement combination in concrete construction

The experimental study reported in this paper was part of a larger comprehensive programme to assess the long-term performance and potential of CSAC-based concretes for new construction with the requirements of design codes. Based on the results, the mechanical and durability properties of the concrete, governed by unique hydration patterns [1], are such that they may meet performance requirements and at the same time reduce the eCO_2 at lower cost than would be associated with the use of conventional PC-based concretes. The determined fresh properties of the CSAC-based concrete investigated were such that they would not normally instigate any risks or concerns during placing, compaction and finishing as the use of polycarboxylate-based superplasticizers appeared to be compatible with the combination. Potentially suitable applications identified for CSAC/anhydrite/fly ash concrete [36] are mainly those under designated XS-2 exposure classes as in BS EN 206: 2013 where sulfate resistance is the predominant parameter and examples include concrete permanently submerged underwater or breakwater applications. In this study, the samples were immersed in a 5% $NaSO_4$ solution, in which the SO_4^{2-} ion concentration was approximately 5.6 times higher than the most aggressive (XA3) class of a 6 g/l concentration. With the CSAC-based concrete exhibiting higher sulfate resistance than PC based concretes at any given w/c ratio, it follows that at any given requirement, its associated eCO_2 would be lower than that of PC concretes in every case.

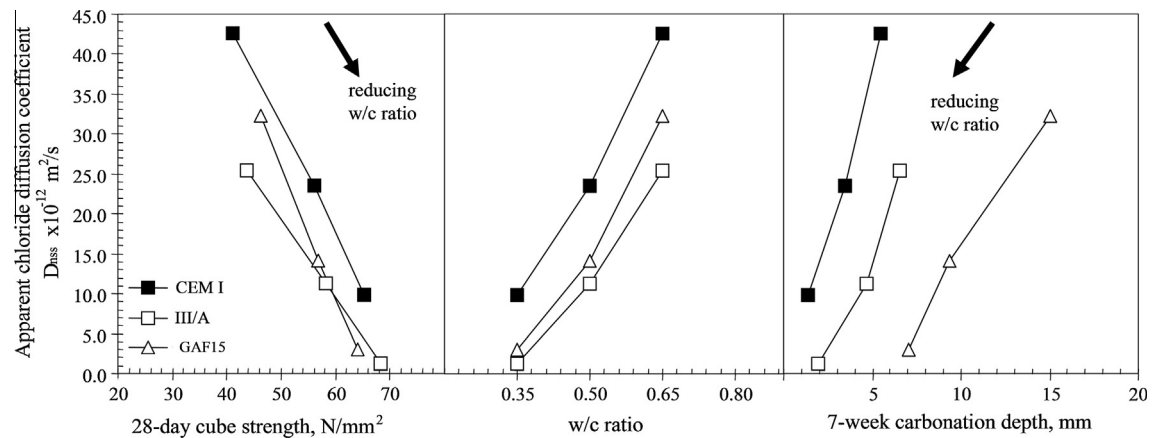


Fig. 10. Non-steady state chloride diffusion coefficients of tested concretes.

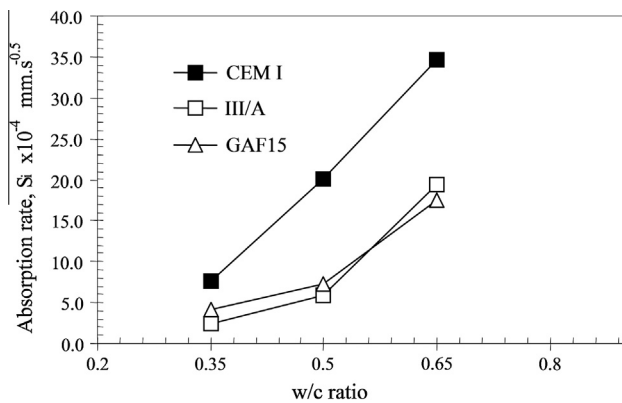


Fig. 11. Relationship between absorption rates of concretes and w/c ratio.

CSAC/anhydrite/fly ash combinations may well be also used in unreinforced concrete structures where a minimum strength class is the predominant requirement; although for reinforced concrete applications such as in XC3/4 designations, an equivalent concrete performance assessment (ECPC) to BS EN 206:2013 is best to be conducted in detail to investigate the balance between performance, cost per volume and eCO_2 , and to assess the extent of conformity with minimum requirements [36]. The principles of ECPC as described in EN 206: 2013 fundamentally ensure the suitability

of a combination-based concrete in a relevant exposure class, such as the CSAC/anhydrite/fly ash combination by implementing a production control. Based on this methodology it is possible to produce appropriate mix designs for satisfying the designation's minimum requirements and for developing controlling mix limitations. By knowing the contents of the constituents in the mix design as well as the individual eCO_2 and cost per m^3 of each, then the total eCO_2 and implicated cost can be determined [36]. Since CSAC/anhydrite/fly ash concrete exhibited poorer carbonation resistance than PC-based concretes tested, it follows that for a given cover lower w/c ratios would be needed to obtain equivalent resistance; consequently higher cement contents would be required. Increasing cement contents are intrinsically associated with increasing eCO_2 and costs and in the case of CSAC/anhydrite fly ash, the yielded combination content is numerically higher than that of PC for achieving a given carbonation resistance. However, this does not necessarily imply that it would also yield higher total eCO_2 and costs than PC.

4. Conclusions

Based on the results, the following points may be summarised:

- The synergistic effect between ettringite and firmly attached FA particles found in previous work [1] creates a cement combination associated with a dense microstructure that is reflected through strong concrete, low chloride diffusion coefficients

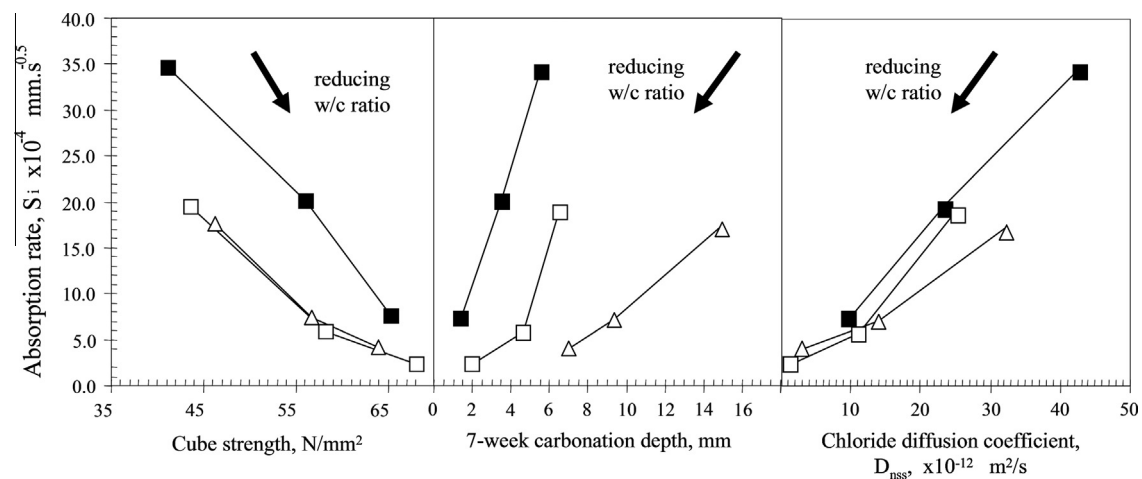


Fig. 12. Water sorptivity rates of tested concretes.

and water absorption rates; although carbonation depths were found to be higher than CEM I -based concretes at a given w/c ratio.

- In conventional Portland cement technology it is evident that the durability of concrete is strongly associated with the w/c ratio of the mix. Although this was found to be true in CSAC/anhydrite/fly ash concretes, it has also been shown that the amount of alkali hydroxides present in the concrete needs to be considered. Such an issue, if neglected, may form the misleading impression that a high-strength CSAC-based concrete should be always associated with high carbonation resistance as in the case of PC concrete.
- Under current design procedures, some potentially suitable applications for CSAC/anhydrite/fly ash concrete include aggressive environments and unreinforced concrete applications. In these cases, the system is most likely to yield lower eCO_2 for satisfying design criteria than when PC concrete would do so, although in designated reinforced concrete this would be defined by determining the balance between eCO_2 , cost and performance that is determined based on the suitability in ECPC.

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